OFFICE OF NAVAL RESEARCH

Contract N00014-91-J-1927

R&T Code 413v001

Technical Report No. 25

ELECTROCHEMICAL PROCESSING OF ELECTRICALLY CONDUCTIVE POLYMER FIBERS

by

SHULONG LI, CHRISTOPHER W. MACOSKO, AND HENRY S. WHITE

Prepared for Publication in

ADVANCED MATERIALS

University of Minnesota
Department of Chemical Engineering and Materials Science
Minneapolis, MN 55455

March 20, 1993

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	March 20, 1993	Technical 6/30/92 - 3/31/93

4. TITLE AND SUBTITLE
ELECTROCHEMICAL PROCESSING OF ELECTRICALLY CONDUCTIVE POLYMER FIBERS

5. FUNDING NUMBERS
N00014-91-J-1927

6. AUTHOR(S)
SHULONG LI, CHRISTOPHER W. MACOSKO, AND HENRY S. WHITE

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Dept. of Chemical Engineering and Materials Science
University of Minnesota

8. PERFORMING ORGANIZATION REPORT NUMBER
Technical Report No. 25

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Unclassified/Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

This article reviews recent developments in the synthesis of electrically conductive composite polymer fibers.

14. SUBJECT TERMS

15. NUMBER OF PAGES
6

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	UL		

Electrochemical Processing of Electrically Conductive Polymer Fibers

Shulong Li*, Christopher W. Macosko*, and Henry S. White**

* Department of Chemical Engineering and Materials Science
University of Minnesota
Minneapolis, MN 55455

** Department of Chemistry
University of Utah
Salt Lake City, UT 84112

The authors gratefully acknowledge support from the Office of Naval Research.

1. Introduction

Electrically conductive polymers, such as polyanaline and polythiophene, have been extensively investigated since the pioneering work of Dall'Olio[1], Lund[2], and Diaz[3] and coworkers on the controlled electrosynthesis of polypyrrole films. Research in this field has been divided relatively evenly among three areas: (i) the development of a fundamental basis for describing charge transport along polymer chains; (ii) the development of novel devices and applications based on the unique optical, electrical, and charge storage properties of these polymers; and (iii) synthesis and processing of conductive polymers with desirable mechanical properties, e.g., flexibility, and chemical robustness.

The focus of our studies has been on the development of an electrochemical process for synthesizing macroscopic fibers of conductive polymers that exhibit mechanical strenght and flexibility. We and others envision that such materials may have applications in light-emitting displays, as electrodes in batteries, or possibly be woven into lightweight electrically-conductive antistatic fabrics.

Submitted to *Advanced Materials*, March, 1993

2. Electrochemical Processing of Conductive Fibers

Conductive heteroaromatic polymers are synthesized by chemical or electrochemical oxidation of the corresponding monomer. An example of this class of reaction is the oxidation of pyrrole in an aqueous solution, eq. (1). Typically, the synthesis yields a

$$x \text{ pyrrole} \rightarrow \text{polypyrrole} + 2x\, e^- + 2x\, H^+ \qquad (1)$$

porous powder, or, for electrochemical oxidation, a thin film attached to the electrode surface. As synthesized, heteroaromatic polymers are electrically conductive, with conductivities ranging from 10^{-3} to 10^{3} $ohm^{-1}cm^{-1}$[4]. Although a few exceptions exist,[5,6,7] the resulting powder or film is insoluble, intractable, or decomposes prior to melting, preventing the use of conventional polymer processing techniques in shaping these materials into desired structures. Thus, applications based on readily assessable optical and electrical properties, but which may require special shapes or mechanical properties, have not been realized.

The problems associated with processing of heteroaromatic polymers may be partially overcome by combining the synthesis and processing steps into a single operation. A straightforward approach is to synthesize the polymer in a form-confining mold, which is subsequently removed to yield the free-standing polymer structure. This strategy has been implemented by Martin and coworkers in the synthesis of polypyrrole fibers of micron dimensions[8]. In their procedure, polypyrrole is electrodeposited within the pores of a thin porous membrane. The membrane is dissolved in an organic solvent exposing the conductive polymeric fibers.

An alternative approach to the processing of polymer fibers is to use hydrodynamic flow patterns to control the direction of growth during polymerization[9]. For example, Fig. 1a shows a flow cell used to synthesize macroscopic fibers of polypyrrole and poly(3-methylthiophene). A solution containing the monomer (e.g., pyrrole) and a supporting

electrolyte are pumped through the cell at a rate corresponding to an average linear velocity between 10 and 100 cm/s. When an electrical current (~1 mA) is passed through the cell such that the monomer is oxidized at the platinum anode, eq. (1), a single conductive fiber nucleates and grows along the central axis of the flow cell at rates approaching 1 cm/hr. Polypyrrole and poly(3-methylthiophene) fibers of 10-cm length and 0.01 to 0.1-cm diameter have been fabricated by this one-step process.

The key element of the above process is the coupling of hydrodynamic flows with mass-transport of the monomer to the fiber surface. The polymerization mechanism not only involves the monomer, but also dimer, trimer, and oligimers (as well as the corresponding radial cations) generated via homogeneous reactions at the surface of the growing fiber. Hydrodynamic flow at the cone-shaped fiber tip produces a relatively stagnant boundary layer, increasing the rate of deposition of intermediates at the tip. Consequently, the polymer preferentially grows in the direction of flow. Since the direction of flow can be readily altered by varying the cell geometry, fibers of arbitrary shape can be processed. For instance, a zigzag shaped fiber can be grown in a zigzags-shaped flow cell[9].

3. Composite Fibers

Single-phase polypyrrole and poly(3-methylthiophene) fibers grown in the electrochemical flow as described above are extremely brittle. Fortunately, conductive composite fibers, which have much improved mechanical properties, can be synthesized in a similar fashion. Fig. 1b shows a flow cell which has been used to prepare electrically conductive Kevlar/polypyrrole composite fibers. The cell is essentially identical to the one used to grow single-phase fibers, Fig. 1a, except that a Kevlar string (comprised of 70 filaments each with a diameter of 17 μm) is suspended in the solution between the anode and cathode. When the solution containing monomer is pumped through the cell and a constant current applied to the electrodes, the polymer is deposited on the platinum anode.

With continued current flow, the polymer grows onto the non-conductive string, rapidly coating the entire length of the Kevlar string at a rate of ~30 cm/hr. Photographs of as-grown and flexed Kevlar/polypyrrole composite fibers are shown in Fig. 2.

The Kevlar/conducting polymer composite fibers have electrical conductivities that are similar to values measured for single-phase fibers. This is largely due to the fact that the polypyrrole is deposited between the filaments of the nonconductive Kevlar string, as demonstrated in the scanning electron micrograph shown in Fig. 3. The flexibility and strength of the composite fibers are greatly improved relative to the single-phase fibers. For instance, Kevlar/polypyrrole fibers can be repeatedly flexed by 180° without any noticable cracking in the vicinity of the bend, and without loss of electrical conductivity.

4. Conclusion

The use of hydrodynamic forces to control the direction of polymer deposition provides a simple method of synthesizing electrically conductive polymer fibers with excellent mechanical properties. Although the methodology is relatively new and understood only at a qualitative level, it may be possible to apply similar processes to the synthesis of non-polymeric materials (e.g., low-dimensional organic conductors or superconducting oxides) which are electrical conductivity and can be synthesized by electrochemically routes.

References

1. A. Dall'Olio, Y. Dascola, V. Varacca, V. Bocchi, *C. R. Hebd, Seances. Acad. Sci. Ser.* **1968**, *C267*, 433.
2. H. Lund, Electrodenreaktioner i Organsik Polarografi og Voltammetri, Aarhus Stiftsbogtrykkorie, Aarhus, **1961**.
3. A. F. Diaz, K. K. Kanazawa, and G. P. Gardini, *J. Chem. Soc., Chem. Comm.* **1979**, 635.
4. J. Heinze, *Top. Curr. Chem.* **1990**, *1*, 152.
5. M. Sato, S. Tanaka, K. Kaeriyama, *Synth. Met.* **1989**, *28*, 229.
6. S.D.D.V. Rughooputh, N. Nowak, S. Hotta, A. J. Heeger, F. Wudl, *Synth. Met.* **1987**, *21*, 41.
7. M. Feldhues, G. Kampf, H. Litterer, T. Mecklenburg, P. Wegener, *Synth. Met.* **1989**, *28*, C487.
8. R. M. Penner, C. R. Martin, *J. Electrochem. Soc.* **1986**, *133*, 2206.
9. S. Li, C. W. Macosko, H. S. White, *Science*, **1993**, *259*, 957.

Figure Captions.

1. Electrochemical flow cells used to grow (a) single-phase polymer fibers and (b) composite fibers.

2. Photographs of Kevlar/polypyrrole composite fibers.

3. SEM image of a Kevlar/polypyrrole composite fiber.